DESCRIPTION

ELECTROLYTIC PROCESSING APPARATUS AND ELECTROLYTIC PROCESSING METHOD

Technical Field

This invention relates to an electrolytic processing apparatus and an electrolytic processing method, and more particularly to an electrolytic processing apparatus and an electrolytic processing method useful for processing a conductive material formed in a surface of a substrate, such as a semiconductor wafer, or for removing impurities adhering to a surface of a substrate.

Background Art

In recent years, instead of using aluminum or aluminum alloys as a material for forming circuits on a substrate such as a semiconductor wafer, there is an eminent movement towards using copper (Cu) which has a low electric resistivity and high electromigration resistance. Copper interconnects are generally formed by filling copper into fine recesses formed in a surface of a substrate. Various techniques for forming such copper interconnects are known including chemical vapor deposition (CVD), sputtering, and plating. According to any such technique, a copper film is formed in a substantially entire surface of a substrate, followed by removal of unnecessary copper by chemical mechanical polishing (CMP).

FIGS. 1A through 1C illustrate, in sequence of process steps, an example of forming such a substrate W having copper interconnects. As shown in FIG. 1A, an insulating film 2, such as an oxide film of SiO_2 or a film of low-k material, is deposited on a conductive layer 1a in which semiconductor devices are formed, which is formed on a semiconductor base 1. Contact holes 3 and interconnect trenches 4 are formed in the insulating film 2 by

the lithography/etching technique. Thereafter, a barrier layer 5 of TaN or the like is formed on the insulating film 2, and a seed layer 7 as an electric supply layer for electroplating is formed on the barrier layer 5 by sputtering or CVD, or the like.

Then, as shown in FIG. 1B, copper plating is performed onto the surface of the substrate W to fill the contact holes 3 and the trenches 4 with copper and, at the same time, deposit a copper film 6 on the insulating film 2. Thereafter, the copper film 6, the barrier layer 5 and the barrier layer 5 on the insulating film 2 are removed by chemical mechanical polishing (CMP) or the like so as to make the surface of the copper film 6 filled in the contact holes 3 and the trenches 4, and the surface of the insulating film 2 lie substantially on the same plane. Interconnects composed of the copper film 6 as shown in FIG. 1C are thus formed.

Components in various types of equipments have recently become finer and have required higher accuracy. As sub-micro manufacturing technology has commonly been used, the properties of materials are largely influenced by the processing method. Under these circumstances, in such a conventional machining method that a desired portion in a workpiece is physically destroyed and removed from a surface thereof by a tool, a large number of defects may be produced to deteriorate the properties of the workpiece. Therefore, it becomes important to perform processing without deteriorating the properties of the materials.

Some special processing methods, such as chemical polishing, electrolytic processing, and electrolytic polishing, have been developed in order to solve this problem. In contrast with the conventional physical processing, these methods perform removal processing or the like through chemical dissolution reaction. Therefore, these methods do not suffer from defects, such as

formation of an altered layer and dislocation, due to plastic deformation, so that processing can be performed without deteriorating the properties of the materials.

In recent years, metals of the platinum group or their oxides have become candidates for an electrode material for use in forming a capacitor, which utilizes a high dielectric material, on a semiconductor substrate. Among them, ruthenium, because of its good film-forming properties and good processibility for patterning, is being progressively studied as a feasible material.

The ruthenium formed on or adhering to the peripheral region or back surface of a substrate, i.e. the non-circuit region of the substrate, is not only unnecessary, but can also cause cross-contamination during later transfer, storage and various processing steps of the substrate, whereby, for instance, the performance of a dielectric material can be lowered. Accordingly, during the process for forming a ruthenium film or after carrying out some treatments of the formed ruthenium film, it is necessary to completely remove the unnecessary ruthenium film. Further, in the case of using ruthenium as an electrode material for forming a capacitor, a step for removing part of a ruthenium film formed on the circuit region of a substrate is needed.

Chemical mechanical polishing (CMP) processing, for example, generally necessitates a complicated operation and control, and needs a considerably long processing time. In addition, a sufficient cleaning of a substrate must be conducted after the polishing treatment. This also imposes a considerable load on the slurry or cleaning waste liquid disposal. Accordingly, there is a strong demand for omitting CMP entirely or reducing a load upon CMP. Also in this connection, it is to be pointed out that though a low-k material, which has a low

dielectric constant, is expected to be predominantly used in the future as a material for the insulating film, the low-k material has a low strength and therefore is hard to endure the stress applied during conventional CMP processing. Thus, also from this standpoint, there is a demand for a process that enables the flattering of a substrate without giving any stress thereto.

Further, when a fragile material, such as a low-k material, is processed in a semiconductor device manufacturing process, there is a fear of destruction of the material due to buckling, etc. It is therefore not possible with such a processing as CMP to apply a high surface pressure between a substrate and a polishing surface, whereby a sufficient polishing cannot be performed. Especially, in these days, it is desired to use copper or a low-dielectric constant material as an interconnect material of a substrate. The above problem becomes remarkable when such a fragile material is used. In the case of electrolytic processing, it is not necessary to apply a surface pressure between a substrate and a processing electrode. It is however possible that a surface pressure is produced when a substrate is brought into contact with a contact member, such as an ion exchanger, covering the processing electrode, which could cause destruction of a semiconductor device. Accordingly, it is necessary even with electrolytic processing to prevent a high load from being applied onto a substrate.

Further, with respect to an electrolytic processing apparatus which performs processing by providing an ion exchanger between a feeding electrode, a processing electrode and a substrate (workpiece) such as a semiconductor wafer, bringing the ion exchanger into contact with the substrate, supplying a fluid, such as ultrapure water, between the electrodes and the ion exchanger and between the ion exchanger and the substrate, and applying a voltage between the feeding electrode and the processing electrode while moving the

electrodes and the substrate relative to each other, variation in the thickness of the ion exchanger, errors in the mounting of the ion exchanger and non-uniformity in the contact pressure between the substrate and the ion exchanger due to the surface configuration of the substrate cause non-uniform processing amount over the entire processing surface and non-uniform surface roughness after processing. Especially, when a multi-layer laminate of ion-exchange membranes (ion exchangers) is used as the ion exchanger in order to increase the ion exchange capacity, the thickness of the ion exchanger is likely to vary with every electrode.

Further, there is also known a chemical-mechanical electrolytic polishing method that carries out CMP simultaneously with plating. According to thus method, mechanical processing is carried out to the growing surface of plating, which can induce abnormal growing of plating that may result in poor quality of the resulting plated film.

In the case of the above-mentioned conventional electrolytic processing or electrolytic polishing, the process proceeds through an electrochemical interaction between a workpiece and an electrolytic solution (aqueous solution of NaCl, $NaNO_3$, HF, HCl, HNO_3, NaOH, etc.). Since an electrolytic solution containing such an electrolyte must be used, contamination of a workpiece with the electrolyte cannot be avoided.

Summary of the Invention

The present invention has been made in view of the above problems in the background art. It is therefore a first object of the present invention to provide an electrolytic processing apparatus and an electrolytic processing method which can perform processing of a substrate without destroying devices formed in the substrate even when a fragile material is employed

in the substrate.

It is a second object of the present invention to provide an electrolytic processing apparatus and an electrolytic processing method which can reduce non-uniformity in the contact pressure of an electrode member against a substrate during processing, thereby further equalizing the processing amount in the entire processing surface of the substrate and the surface roughness after processing.

It is a third object of the present invention to provide an electrolytic processing apparatus which can process a conductive material on a substrate into a flat surface while omitting CMP entirely or at least reducing the load on CMP, or can remove (clean off) matter adhering to the surface of a workpiece such as a substrate.

In order to achieve the above object, the present invention provides an electrolytic processing apparatus comprising: a substrate holder for holding a substrate; an electrode base provided with a electrode member for contact with the substrate, held by the substrate holder, in the presence of a liquid to effect processing of the substrate; and a support base for floatingly supporting the electrode base by a floating mechanism.

FIGS. 2 and 3 illustrate the principle of processing according to the present invention. FIG. 2 shows the ionic state in the reaction system when an ion exchanger 12a mounted on a processing electrode 14 and an ion exchanger 12b mounted on a feeding electrode 16 are brought into contact with or close to a surface of a workpiece 10, while a voltage is applied from a power source 17 to between the processing electrode 14 and the feeding electrode 16, and a fluid 18, such as ultrapure water, is supplied from a fluid supply section 19 to between the processing electrode 14, the feeding electrode 16 and the workpiece 10. FIG. 3 shows the ionic state in the reaction system

when the ion exchanger 12a mounted on the processing electrode 14 is brought into contact with or close to the surface of the workpiece 10 and the feeding electrode 16 is directly contacted with the workpiece 10, while a voltage is applied from the power source 17 to between the processing electrode 14 and the feeding electrode 16, and the fluid 18, such as ultrapure water, is supplied from the fluid supply section 19 to between the processing electrode 14 and the workpiece 10.

When using a liquid, like ultrapure water, which itself has a large resistivity, it is preferred to bring the ion exchanger 12a into "contact" with the surface of the workpiece 10. This can lower the electric resistance, lower the voltage applied, and reduce the power consumption. Thus, the "contact" in the processing according to the present invention does not imply "press" for giving a physical energy (stress) to a workpiece as in CMP.

In FIGS. 2 and 3, water molecules 20 in the fluid 18, such as ultrapure water, are dissociated by the ion exchangers 12a and 12b into hydroxide ions 22 and hydrogen ions 24. The hydroxide ions 22 thus produced, for example, are carried, by the electric field between the workpiece 10 and the processing electrode 14 and by the flow of the fluid 18, to the surface of the workpiece 10 facing the processing electrode 14, whereby the density of the hydroxide ions 22 in the vicinity of the workpiece 10 is increased, and the hydroxide ions 22 are reacted with the atoms 10a of the workpiece 10. The reaction product 26 produced by reaction is dissolved in the fluid 18 such as ultrapure water, and removed from the workpiece 10 by the flow of the fluid 18 along the surface of the workpiece 10. Removal processing of the surface layer of the workpiece 10 is thus effected.

As will be appreciated from the above, the removal processing according to the present method is effected purely

by the electrochemical interaction between the reactant ions and the workpiece. According to the present method, the portion of the workpiece 10 facing the processing electrode 14 is processed. Therefore, by moving the processing electrode 14, the workpiece 10 can be processed into a desired surface configuration.

Further, since the electrolytic processing apparatus according to the present invention performs processing with lower pressure as compared to a conventional CMP apparatus, the present electrolytic processing apparatus can perform removal processing of a material without impairing the properties of the material. Even when the material is of a low mechanical strength, such as the above-described low-k material, removal processing of the material can be effected. Further, as compared to conventional electrolytic processing apparatuses, the apparatus of the present invention, because of the use as a processing liquid a liquid having an electric conductivity of not more than 500 μS/cm, preferably pure water, more preferably ultrapure water, can remarkably reduce contamination of the surface of a workpiece with impurities and can facilitate disposal of waste liquid after the processing. The present invention can be applied to electrolytic processing using an electrolytic solution or a chelating agent, or the like, and contact electrolytic processing, such as composite electrolytic processing using an abrasive agent or a slurry.

According to this electrolytic processing apparatus, the electrode base provided with the electrode member is supported floatingly and can be tilted by the force applied thereto from the substrate via the electrode member, so that the electrode member can contact the substrate more uniformly over a wider area of the substrate. This makes it possible to equalize the contact pressure of the electrode member on the substrate even when there is a variation in the configuration of the electrode

member.

Preferably, the electrolytic processing apparatus further comprises a stopper for limiting the movements of the electrode base in a direction away from the support base and in a direction parallel to the support base.

Such a stopper can prevent the electrode base from escaping from the support base in a non-processing time when the electrode member is not in contact with a substrate, and also prevent the electrode base from moving in a direction parallel to the support base due to a fictional force generated between the electrode member and the substrate during processing.

In a preferred embodiment of the present invention, the floating mechanism supports the electrode base floatingly by an elastic body interposed between the electrode base and the support base.

The electrode base can be tilted through the elastic force of the elastic body so that the electrode member can contact a substrate more uniformly over a wider area of the substrate.

The floating mechanism may also support the electrode base by the pressure of a fluid enclosed within a pressure chamber formed between the electrode base and the support base, and surrounded by an elastic membrane.

The electrode base can be tilted through the pressure of a fluid enclosed within the pressure chamber, which is formed between the electrode base and the support base and surrounded by an elastic membrane, so that the electrode member can contact a substrate more uniformly over a wider area of the substrate.

Preferably, the fluid at a predetermined pressure is supplied into the pressure chamber.

The pressure of the fluid may be adjusted so that the pressure applied to the substrate from the electrode member (electrode or ion exchanger) becomes not more than 19.6 kPa (200 gf/cm^2, 2.9 psi), preferably not more than 6.86 kPa (70 gf/cm^2, 1.0 psi),

more preferably not more than 686 Pa (7 gf/cm^2, 0.1 psi). By thus adjusting the pressure of the fluid to be supplied into the pressure chamber, the pressure between the substrate and the electrode member upon their contact can be controlled as desired. Thus, the interfacial pressure between the substrate and the electrode member can be controlled at a lower pressure than a pressure at which a semiconductor device can be destroyed, enabling processing of the substrate without destroying a fragile material.

It is preferred that a plurality of electrodes be fixed on the electrode base.

The present invention provides another electrolytic processing apparatus comprising: a substrate holder for holding a substrate; an electrode member for contact with the substrate, held by the substrate holder, in the presence of a liquid to effect processing of the substrate; and an electrode support base for floatingly supporting the electrode member by a floating mechanism.

According to this electrolytic processing apparatus, the electrode member is supported floatingly and can be tilted by the force applied thereto from the substrate, so that the electrode member can contact the substrate more uniformly over a wider area of the substrate. This makes it possible to equalize the contact pressure of the electrode member on the substrate even when there is a variation in the configuration of the electrode member.

Preferably, the electrode member is provided in numbers and each electrode member is supported floatingly by an independent floating mechanism.

This makes it possible to floatingly support each electrode member independently.

Preferably, the electrolytic processing apparatus further comprises a stopper for limiting the movements of the electrode

member in a direction away from the electrode support base and in a direction parallel to the electrode support base.

Such a stopper can prevent the electrode member from escaping from the electrode support base in a non-processing time when the electrode member is not in contact with a substrate, and also prevent the electrode member from moving in a direction parallel to the electrode support base due to a fictional force generated between the electrode member and the substrate during processing.

In a preferred embodiment of the present invention, the floating mechanism supports the electrode member floatingly by an elastic body interposed between the electrode member and the electrode support base.

The electrode support base can be tilted through the elastic force of the elastic body so that the electrode member can contact a substrate more uniformly over a wider area of the substrate.

The floating mechanism may also support the electrode member by the pressure of a fluid enclosed within a pressure chamber formed between the electrode member and the electrode support base, and surrounded by an elastic membrane.

The electrode member can be tilted through the pressure of a fluid enclosed within the pressure chamber, which is formed between the electrode member and the electrode support base and surrounded by an elastic membrane, so that the electrode member can contact a substrate more uniformly over a wider area of the substrate.

Preferably, the fluid at a predetermined pressure is supplied into the pressure chamber.

The pressure of the fluid may be adjusted so that the pressure applied to the substrate from the electrode member (electrode or ion exchanger) becomes not more than 19.6 kPa (200 gf/cm^2, 2.9 psi), preferably not more than 6.86 kPa (70 gf/cm^2, 1.0 psi), more preferably not more than 686 Pa (7 gf/cm^2, 0.1 psi). By

thus adjusting the pressure of the fluid to be supplied into the pressure chamber, the pressure between the substrate and the electrode member upon their contact can be controlled as desired. Thus, the interfacial pressure between the substrate and the electrode member can be controlled at a lower pressure than a pressure at which a semiconductor device can be destroyed, enabling processing of the substrate without destroying a fragile material.

It is preferred that the electrode member includes an electrode to be connected to a power source, and an ion exchanger or a scrubbing member covering a surface of the electrode.

The present invention provides yet another electrolytic processing apparatus comprising: a substrate holder for holding a substrate; a plurality of electrode members for contact with the substrate, held by the substrate holder, in the presence of a liquid to effect processing of the substrate; a floating mechanism for floatingly supporting the electrode members; and an adjustment member for floating a part of the plurality of electrode members selectively or changing the elasticity, which is generated by the floating mechanism, of a part of the plurality of electrode members.

According to this electrolytic processing apparatus, processing of a substrate can be carried out while allowing the electrode member to be in contact with the substrate with a low elasticity (low modulus of elasticity) so that the interfacial pressure upon contact of the electrode member with the substrate is low.

The adjustment member is preferably provided to a feeding electrode member for feeding electricity to the substrate.

The present invention provides yet another electrolytic processing apparatus comprising: a substrate holder for holding a substrate; an electrode member for contact with the substrate, held by the substrate holder, in the presence of a liquid to

effect processing of the substrate; a drive mechanism for moving the substrate, held by the substrate holder, and the electrode member relative to each other; and a guide member disposed around the substrate holder and having an outwardly-extending tapered guide surface which, upon the relative movement between the substrate and the electrode member, comes into contact with the upper surface of the electrode member and guides the electrode member to a contact position at which the electrode member makes contact with the substrate.

The provision of the guide member, when positioning the electrode member at a contact position for contact with the substrate during the relative movement between the electrode member and the substrate, can prevent the electrode member from colliding against the peripheral end surface of the substrate and facilitate smooth movement of the electrode member.

The present invention provides yet another electrolytic processing apparatus comprising: a substrate holder for holding a substrate; an electrode member for contact with the substrate, held by the substrate holder, in the presence of a liquid to effect processing of the substrate; a drive mechanism for moving the substrate, held by the substrate holder, and the electrode member relative to each other; and a guide member disposed around the substrate holder and having a contact surface which comes into contact with the electrode member outside the substrate; wherein the contact area of the electrode member with the guide member and the substrate is constant.

According to this electrolytic processing apparatus, the electrode member, besides its contact with the substrate, makes contact with the contact surface of the guide member outside the substrate, so that the contact area of the electrode member with the substrate and the contact surface of the guide member is constant even when the relative position between the substrate and the electrode member is changing during the relative movement.

This prevents the pressure between the electrode member and the substrate in the contact portion from changing locally.

Preferably, the electrode member includes an electrode to be connected to a power source, and an ion exchanger or a scrubbing member covering the surface of the electrode.

The use of an ion exchange in carrying out electrolytic processing can promote the dissociation of water molecules in a liquid, such as ultrapure water, into hydroxide ions and hydrogen ions. Further, it is possible to allow a substrate to make contact with the ion exchanger, avoiding contact of the substrate with an electrode. The use of a scrubbing member, on the other hand, can remove a metal oxide or a chelate film on the surface of a material to be processed.

Preferably, the electrode member is provided in numbers, and the outer shape of the guide member is similar to the outer shape defined by the electrode members which are in contact with the substrate held by the substrate holder.

The present invention also provides an electrolytic processing method comprising: bringing a substrate into contact with an electrode member mounted on a floatingly-supported electrode base in the presence of a liquid while moving the substrate and the electrode member relative to each other, thereby processing the surface of the substrate.

The present invention provides another electrolytic processing method comprising: bringing a substrate into contact with a floatingly-supported electrode member in the presence of a liquid while moving the substrate and the electrode member relative to each other, thereby processing the surface of the substrate.

The present invention provides yet another electrolytic processing method comprising: bringing a substrate, held by a substrate holder, into contact with an electrode member in the presence of a liquid while moving the substrate and the electrode

member relative to each other; and bringing the upper surface of the electrode member into contact with a guide surface of a guide member disposed around the substrate to guide the electrode member to a contact position at which the electrode member makes contact with the substrate held by the substrate holder, during the relative movement between the substrate and the electrode member, thereby processing the surface of the substrate.

The present invention provides yet another electrolytic processing method comprising: bringing a substrate, held by a substrate holder, into contact with an electrode member in the presence of a liquid while moving the substrate and the electrode member relative to each other; and bringing the electrode member into contact with a contact surface of a guide member, disposed around the substrate holder, such that the contact area of the electrode member with the contact surface and the substrate is constant.

The present invention provides yet another electrolytic processing apparatus comprising: an electrode section provided with an electrode member including an electrode and an ion exchanger covering a surface of the electrode; a holder for holding a workpiece, capable of bringing the workpiece close to or into contact with the ion exchanger of the electrode member; and a power source to be connected to the electrode of the electrode member of the electrode section; wherein at least an edge portion of the surface, facing the workpiece, of the electrode is made round.

When an ion exchanger is provided such that it covers an electrode and processing of a workpiece is carried out by applying a voltage between electrodes (processing electrode and feeding electrode), the electric field concentrates on the edge portion of the surface, facing the workpiece, of the electrode. The processing products produced by electrolytic reaction (copper

ions and copper hydroxide) are taken and accumulated preferentially in the portion of the ion exchanger in contact with the electrode edge portion on which the electric field concentrates. Accordingly, the accumulation amount of the processing products increases more in the edge portion of the ion exchanger as compared to the other portion. After the accumulation amount of the processing products in one portion has reached the ion-exchanger capacity, electrons that participate in the ion-exchange reaction are supplied to the workpiece, not via the surface of the ion exchanger, but via the reaction products accumulated in the ion exchanger, whereby the dissociation reaction of water molecules does not occur or reduces significantly. Thus, the ion exchanger cannot attain the intended effect of removing a processing object on the workpiece, nor can make best use of the ion-exchange capacity of a portion with less accumulation of the reaction products.

According to the present invention, at least the edge portion of the workpiece-facing surface of the electrode is made round. This can lessen the electric field concentration and can therefore reduce the above-described local accumulation of processing products, thereby extending the life of the ion exchanger.

Preferably, the electrode is provided in numbers, and the electrodes are arranged in parallel in the electrode section. Preferably, each electrode has a rectangular cross-section, and the workpiece-facing surface has a semicircular shape. When a long electrode with a narrow width is used, by making the entire workpiece-facing surface semicircular, it becomes possible to reduce the local accumulation of processing products in the ion exchanger covering the electrode and narrow that area of the ion exchanger which is to come close to or into contact with a workpiece.

The electrodes may have a circular cross-section, and

arranged in parallel in the electrode section. The use of a long electrode having a circular cross-section can also reduce the local accumulation of processing products in the ion exchanger covering the electrode and narrow that area of the ion exchanger which is to come close to or into contact with a workpiece.

The present invention provides yet another electrolytic processing apparatus comprising: an electrode section provided with an electrode member including an electrode and an ion exchanger covering a surface of the electrode; a holder for holding a workpiece, capable of bringing the workpiece close to or into contact with the ion exchanger of the electrode member; and a power source to be connected to the electrode of the electrode member of the electrode section; wherein an insulator is interposed between the ion exchanger and the surface, facing the workpiece, of the electrode.

When an ion exchanger is provided such that it covers an electrode and processing of a workpiece is carried out by applying a voltage between electrodes (processing electrode and feeding electrode), the electric field concentrates on the portion of the electrode at which the distance from the workpiece is smallest, i.e. the workpiece-facing surface. The processing products produced by electrolytic reaction (copper ions and copper hydroxide) are taken and accumulated preferentially in the workpiece-facing portion of the ion exchanger on which the electric field concentrates. Accordingly, the accumulation amount of the processing products increases more in the workpiece-facing portion of the ion exchanger as compared to the other portion. After the accumulation amount of the processing products in one portion has reached the ion-exchanger capacity, electrons that participate in the ion-exchange reaction are supplied to the workpiece, not via the surface of the ion exchanger, but via the reaction products accumulated

in the ion exchanger, whereby the dissociation reaction of water molecules does not occur or reduces significantly. Thus, the ion exchanger cannot attain the intended effect of removing a processing object on the workpiece, nor can make best use of the ion-exchanger capacity of a portion with less accumulation of the reaction products.

According to the present invention, an insulator is interposed between the workpiece-facing surface of the electrode and the ion exchanger. This can eliminate the electric field concentration on the workpiece-facing surface of the electrode and can therefore reduce the local accumulation of processing products, thereby extending the life of the ion exchanger. Further, according to necessity, the distance between a workpiece and the contact portion of the ion exchanger with the electrode on which the electric field concentrates may be larger by an insulator, and the ion exchanger volume between the electric field concentration portion and the workpiece may be increased. This can also extend the life of the ion exchanger.

It is preferred that the electrode and the insulator be formed integrally.

This makes it possible to easily produce an electrode provided with an insulator which has a desired height (thickness) and provides a desired distance between the electric field concentration portion and a workpiece.

The present invention provides yet another electrolytic processing apparatus comprising: an electrode section provided with an electrode member including an electrode and an ion exchanger covering a surface of the electrode; a holder for holding a workpiece, capable of bringing the workpiece close to or into contact with the ion exchanger of the electrode member; and a power source to be connected to the electrode of the electrode member of the electrode section; wherein the ion exchanger comprises an ion exchanger to be close to or in contact

with the workpiece, and at least one other ion exchanger, and the electrode and the ion exchanger to be close to or in contact with the workpiece are at least partly insulated from each other by an insulator.

In the case of using a composite ion exchanger comprising a plurality of ion exchangers, if an ion exchanger to be close to or in contact with a workpiece is in direct contact with an electrode, an electric current flows preferentially in the ion exchanger, and therefore the processing products accumulate locally in the ion exchanger in a concentrated manner. This makes it impossible to make best use of the total ion-exchange capacity of the composite ion exchanger including the other ion exchanger(s). This drawback is marked especially with a thin ion-exchange membrane having a small ion-exchange capacity, such as Nafion (trademark, DuPont Co.).

According to the present invention, the electrode and the ion exchanger to be close to or in contact with a workpiece are at least partly insulated from each other by an insulator. This can prevent an electric current from flowing preferentially in the ion exchanger which is close to or in contact with the workpiece, thereby extending the life of the composite ion exchanger.

The insulator is preferably interposed between the edge portion of the surface, facing the workpiece, of the electrode and the ion exchanger to be close to or in contact with the workpiece.

It is preferred that the electrode and the insulator be formed integrally. This facilitates the production of the electrode provided with the insulator.

The present invention provides yet another electrolytic processing apparatus comprising: an electrode section provided with an electrode member including an electrode and an ion exchanger covering a surface of the electrode; a holder for

holding a workpiece, capable of bringing the workpiece close to or into contact with the ion exchanger of the electrode member; and a power source to be connected to the electrode of the electrode member of the electrode section. The ion exchanger comprises an ion exchanger to be close to or in contact with the workpiece, and at least one other ion exchanger, and the ion exchanger to be close to or in contact with the workpiece and the at least one other ion exchanger are at least partly insulated from each other by an insulator.

When a composite ion exchanger comprising a plurality of ion exchangers is employed, the accumulation or growth of processing products proceeds preferentially in an ion exchanger in contact with the electrode. If an ion exchanger, which is close to or in contact with a workpiece, is in contact with another ion exchanger (for example, the ion exchanger in contact with the electrode), the processing products accumulated in another ion exchanger spreads into the ion exchanger close to or in contact with the workpiece. When the processing products grow and pass through the surface of the ion exchanger and reach the workpiece, a short circuit will occur. It is thus not possible to make best use of the ion-exchange capacity of the composite ion exchanger.

According to the present invention, the ion exchanger to be close to or in contact with a workpiece and other ion exchanger(s) are at least partly insulated. This can prevent the processing products accumulated in the other ion exchanger(s) from diffusing into the ion exchanger close to or in contact with the workpiece, thereby extending the life of the composite ion exchanger.

Preferably, the at least one other ion exchanger, except its surface facing the workpiece, is surrounded integrally by the insulator.

Brief Description of Drawings

FIGS. 1A through 1C are diagrams illustrating, in sequence of process steps, an example of a production of a substrate with copper interconnects;

FIG. 2 is a diagram illustrating the principle of electrolytic processing according to the present invention as carried out by bringing a processing electrode and a feeding electrode, both having an ion exchanger mounted thereon, closed to a substrate (workpiece), and supplying pure water or a liquid having an electric conductivity of not more than 500 μS/cm between the processing electrode, the feeding electrode and the substrate (workpiece);

FIG. 3 is a diagram illustrating the principle of electrolytic processing according to the present invention as carried out by mounting the ion exchanger only on the processing electrode and supplying the fluid between the processing electrode and the substrate (workpiece);

FIG. 4 is a plan view showing the construction of a substrate processing apparatus provided with an electrolytic processing apparatus according to an embodiment of the present invention;

FIG. 5 is a plan view schematically showing the electrolytic processing apparatus of the substrate processing apparatus shown in FIG. 4;

FIG. 6 is a sectional front view of the electrolytic processing apparatus of FIG. 5;

FIG. 7 is a sectional left-side view of the electrolytic processing apparatus of FIG. 5;

FIG. 8A is a graph showing the relationship between electric current and time, as observed in electrolytic processing of the surface of a substrate having a film of two different materials formed in the surface, and FIG. 8B is a graph showing the relationship between voltage and time, as observed in electrolytic processing of the surface of a substrate having

a film of two different materials formed in the surface;

FIG. 9 is a sectional front view of an electrolytic processing apparatus according to another embodiment of the present invention;

FIG. 10 is a sectional view taken along the line A-A of FIG. 9;

FIG. 11 is a sectional front view of an electrolytic processing apparatus according to yet another embodiment of the present invention;

FIG. 12 is a cross-sectional view of an electrolytic processing apparatus according to yet another embodiment of the present invention;

FIG. 13 is an enlarged view of a portion of FIG. 12,

FIG. 14 is a vertical sectional view of an electrolytic processing apparatus according to yet another embodiment of the present invention;

FIG. 15A is a plan view of a rotation-prevention mechanism of the electrolytic processing apparatus of FIG. 14, and FIG. 15B is a sectional view taken along the line A-A of FIG. 15A;

FIG. 16 is a plan view of the electrode section of the electrolytic processing apparatus of FIG. 14;

FIG. 17 is a sectional view taken along the line B-B of FIG. 16;

FIG. 18 is an enlarged view of a portion of FIG. 17;

FIG. 19 is a cross-sectional diagram illustrating an electrode member consisting of an electrode, not having a round edge portion in the surface facing a substrate, and an ion exchanger covering the surface of the electrode;

FIGS. 20A through 20C are cross-sectional diagrams illustrating the main portions of various electrode members for use in an electrolytic processing apparatus according to yet another embodiment of the present invention;

FIGS. 21A through 21D are cross-sectional diagrams

illustrating the main portions of various electrode members for use in an electrolytic processing apparatus according to yet another embodiment of the present invention;

FIG. 22 is a cross-sectional diagram illustrating the main portion of an electrode member for use in an electrolytic processing apparatus according to yet another embodiment of the present invention;

FIG. 23 is a cross-sectional diagram illustrating an electrode member which uses a plurality of ion exchangers and in which the outer ion exchanger to be close to or in contact with a substrate is in contact with an electrode; and

FIGS. 24A through 24C are cross-sectional diagrams illustrating the main portions of various electrode members for use in an electrolytic processing apparatus according to yet another embodiment of the present invention.

Detailed Description of the Invention

Preferred embodiments of the present invention will now be described with reference to the drawings. Though the below-described embodiments apply to electrolytic processing apparatuses that use a substrate as a workpiece to be processed and process the substrate, the present invention is of course applicable to other workpieces besides the substrate.

FIG. 4 is a plan view illustrating a construction of a substrate processing apparatus provided with an electrolytic processing apparatus according to an embodiment of the present invention. As shown in FIG. 4, the substrate processing apparatus comprises a pair of the loading/unloading units 30 as a carry-in and carry-out section for carrying in and carrying out a cassette housing a substrate W, e.g. a substrate W, as shown in FIG. 1B, which has in its surface a copper film 6 as a conductive film (to-be-processed film), a reversing machine 32 for reversing the substrate W, an electrolytic processing

apparatus 34, and a cleaning section 39 for cleaning and drying the processed substrate. These devices are disposed in series. A transport robot 36 as a transport device, which can move parallel to these devices for transporting and transferring the substrate W therebetween, is provided. The substrate processing apparatus is also provided with a monitor 38, adjacent to the loading/unloading units 30, for monitoring a voltage applied between the below-described processing electrodes and the feeding electrodes upon electrolytic processing in the electrolytic processing apparatus 34, or an electric current flowing therebetween. The substrate processing apparatus may be provided with a CMP section.

FIG. 5 is a plan view schematically showing the electrolytic processing apparatus 34 shown in FIG. 4, FIG. 6 is a sectional front view (direction of arrow Y) of FIG. 5, and FIG. 7 is a sectional left-side view (direction of arrow X) of FIG 5. As shown in FIGS. 6 and 7, the electrolytic processing apparatus 34 according to this embodiment includes a arm 40 that can move vertically and make a reciprocation movement in a horizontal plane, a substrate holder 42, supported at the free end of the arm 40, for attracting and holding the substrate W with its front surface facing downwardly (face-down), moveable flame 44 to which the arm 40 is attached, a rectangular electrode section 46, and a power source 48 to be connected to the electrode section 46.

A vertical-movement motor 50 is mounted on the upper end of the moveable flame 44. A ball screw 52, which extends vertically, is connected to the vertical-movement motor 50. The base 40a of the arm 40 is connected to a ball screw 52, so that the arm 40 moves up and down via the ball screw 52 by the actuation of the vertical-movement motor 50. The moveable flame 44 is connected to a ball screw 54 that extends horizontally, so that the moveable flame 44 moves back-and-forth in a horizontal plane

with the arm 40 by the actuation of a reciprocating motor 56.

The substrate holder 42 is connected to a substrate-rotating motor 58 supported at the free end of the arm 40. The substrate holder 42 is rotated by the actuation of the substrate-rotating motor 58. The arm 40 can move vertically and make a reciprocation movement in the horizontal direction, as described above. The substrate holder 42 can move vertically and make a reciprocation movement in the horizontal direction integrated with the arm 40.

Next, the electrode section 46 according to this embodiment will now be described. The electrode section 46 includes a plurality of electrode members 60 which extend in the X direction (see FIG. 5), and are disposed in parallel at an even pitch on a rectangular tabular electrode base 62. As shown in FIG. 7, each electrode member 60 comprises an electrode 64 to be connected to a power source 48, and an ion exchanger (ion exchange membrane) 66 covering a surface of the electrode 64 integrally.

According to this embodiment, the electrodes 64 of adjacent electrode members 60 are connected alternately to the cathode and to the anode of the power source 48. Electrodes 64 connected to the cathode of the power source 48 became processing electrodes 64a (see FIG. 7), and electrodes 64 connected to the anode of the power source 48 become feeding electrodes 64b (see FIG. 7). When processing copper, for example, the electrolytic processing action occurs on the cathode side, and therefore the electrodes 64 connected to the cathode become processing electrodes 64a, and the electrodes 64 connected to the anode become feeding electrodes 64b. Thus, according to this embodiment, the processing electrodes 64a and the feeding electrodes 64b are disposed in parallel and alternately.

Depending upon the material to be processed, the electrode connected to the cathode of the power source may serve as a feeding electrode, and the electrode connected to the anode may serve

as a processing electrode. Thus, when the material to be processed is copper, molybdenum, iron, or the like, the electrolytic processing action occurs on the cathode side, and therefore the electrode 64 connected to the cathode of the power source 48 becomes a processing electrode 64a, and the electrode 64 connected to the anode becomes a feeding electrode 64b. On the other hand, when the material to be processed is aluminum, silicon, or the like, the electrolytic processing action occurs on the anode side, and therefore the electrode connected to the anode of the power source becomes a processing electrode and the electrode connected to the cathode becomes a feeding electrode.

By thus providing the processing electrodes 64a and the feeding electrodes 64b alternately in the Y direction of the electrode section 46 (direction perpendicular to the long direction of the electrode members 60), provision of a feeding section for feeding electricity to the conductive film (to-be-processed film) of the substrate W is no longer necessary, and processing of the entire surface of the substrate becomes possible. Further, by changing the voltage applied between the electrodes 64 in a pulse form (preferably square wave composed of a positive electrical potential and a zero electrical potential), it becomes possible to dissolve the electrolysis products, and improve the flatness of the processed surface through the multiplicity of repetition of processing.

With respect to the electrodes 64 of the electrode members 60, oxidation or dissolution thereof due to an electrolytic reaction may be a problem. In view of this, as a material for the electrode, it is possible to use, besides the conventional metals and metal compounds, carbon, relatively inactive noble metals, conductive oxides or conductive ceramics. A noble metal-based electrode may, for example, be one obtained by plating or coating platinum or iridium onto a titanium that is

used as an electrode base material, and then sintering the coated electrode at a high temperature to stabilize and strengthen the electrode. Ceramics products are generally obtained by heat-treating inorganic raw materials, and ceramics products having various properties are produced from various raw materials including oxides, carbides and nitrides of metals and nonmetals. Among them there are ceramics having an electric conductivity. When an electrode is oxidized, the value of the electric resistance generally increases to cause an increase of applied voltage. However, by protecting the surface of an electrode with a non-oxidative material such as platinum or with a conductive oxide such as an iridium oxide, the decrease of electric conductivity due to oxidation of the base material of an electrode can be prevented.

A flow passage (not shown), connected to a pure water supply source, is formed in the interior of the electrode base 62 of the electrode section 46. On either side of each electrode member 60 is provided pure water supply nozzles 68 each having inside vertically-extending through-holes 68a which communicate with the flow passage. Pure water, preferably ultrapure water, is thus supplied through the through-holes 68a to between the substrate W and the ion exchangers 66 of the electrode members 60. The height of the pure water supply nozzle 68 is set to be lower than the electrode member 60 so as to avoid contact of the pure water supply nozzle 68 with the substrate W upon electrolytic processing. It is also possible to mount a buffer member, formed of a material having such an elasticity as not to scratch the surface of the substrate W, on the upper surface of the pure water supply nozzle 68, as shown in FIGS. 12 and 13, and allow the buffer member to make contact with the substrate. Specific examples of such a buffer member include POLYTEX pad (trademark, Rodel, Inc.), a polyurethane sponge, a non-woven fabric, a foamed polyurethane, and a PVA sponge.

The electrode base 62 is supported floatingly on a support base 70 by a floating mechanism 72. The floating mechanism 72 includes a pressure chamber 76 formed between the electrode base 62 and the support base 70 and surrounded by an elastic membrane 74, and a pressurized fluid supply passage 81 extending from a pressurized fluid supply source 78 and communicating with the pressure chamber 76. The floating mechanism 72 also includes a fluid pressure control section 83 for controlling the pressure of the fluid to be supplied from the pressurized fluid supply source 78. Thus, the fluid at a controlled pressure is supplied from the pressurized fluid supply passage 81 into the pressure chamber 76, so that the electrode base 62 is supported floatingly by the fluid pressure of the fluid enclosed within the pressure chamber 76.

By thus supporting the electrode base 62, provided with the electrode members 60 each consisting of the electrode 64 and the ion exchanger (contact member) 66, floatingly on the support base 70, the electrode base 62 can be tilted by the force applied thereto from the substrate W via the electrode members 60, so that the electrode members 60 can make contact with the substrate W more uniformly over a wider area of the substrate W. This makes it possible to equalize the contact pressures of the electrode members 60 on the substrate W even when there is variation in the thickness of the ion exchanger 66, errors in the mounting of the ion exchanger 66, etc.

Further, by adjusting the pressure of the fluid to be supplied into the pressure chamber 76 with the above-described adjustment member, the pressure between the substrate W and the electrode member 60 upon their contact can be controlled as desired. Thus, the interfacial pressure between the substrate W and the electrode member 60 can be controlled at a lower pressure than a pressure at which a semiconductor device can be destroyed, enabling processing of the substrate without destroying a

fragile material.

On the peripheral portion of the support base 70 is vertically mounted a stopper 85, in a rectangular shape conforming to the outer shape of the electrode base 62, for limiting the upward movement and the horizontal movement of the electrode base 62. In particular, the stopper 85 has at its upper end an inwardly-projecting expanded portion 85a, while the electrode base 62 has at its peripheral end a step portion 62a. The upward movement of the electrode base 62 is limited by engagement between the expanded portion 85a and the step portion 62a. On the other hand, by sliding contact between the inner circumferential surface of the expanded portion 85a and the outer circumferential surface of the smaller-diameter portion, above the step portion 62a, of the electrode base 62, the horizontal movement of the electrode base 62 is limited without the tilting movement of the electrode base 62 being impeded.

Such a stopper 85 can prevent the electrode base 62 from escaping from the support base 70 in a non-processing time when the electrode members 60 are not in contact with the substrate W, and can also prevent the electrode base 62 from moving in a direction parallel to the support base 70 due to a frictional force generated between the ion exchangers 66 of the electrode members 60 and the substrate W during processing.

Next, substrate processing (electrolytic processing) by using the substrate processing apparatus provided with the electrolytic processing apparatus 34 of this embodiment will be described. First, a substrate W, e.g. a substrate W, as shown in FIG. 1B, which has in its surface a copper film 6 as a conductive film (to-be-processed film), is taken by the transport robot 36 out of the cassette housing substrates and set in the loading/unloading section 30. If necessary, the substrate W is transferred to the reversing machine 32 by the transport robot

36 to reverse the substrate W so that the front surface of the substrate W having the conductor film (copper film 6) faces downwardly.

The transport robot 36 receives the reversed substrate W and transfers it to the electrolytic processing apparatus 34. The substrate W is attracted and held by the substrate holder 42. Then the arm 40 is moved to move the substrate holder 42 holding the substrate W to a processing position right above the electrode section 46. Next, the vertical-movement motor 50 is driven to lower the substrate holder 42 so as to bring the substrate W held by the substrate holder 42 into contact with the surfaces of the ion exchangers 66 of the electrode section 46.

Upon this contact, a fluid at a predetermined pressure is supplied into the pressure chamber 76 of the electrode section 46, whereby the electrode base 62 can be tilted so that the ion exchangers 66 of the electrode members 66 can contact the substrate W more uniformly over the entire surface of the substrate W and the contact pressure of the ion exchangers 66 of the electrode members 60 on the substrate W can be equalized.

Thereafter, the substrate-rotating motor 58 is driven to rotate the substrate W with the substrate holder 42 and, at the same time, the reciprocating motor 56 is driven to allow the substrate W with the substrate holder 42 to make a reciprocation movement in the Y direction shown in FIG. 5. At this time, pure water or ultrapure water is supplied through the pure water supply nozzles 68 to between the substrate W and the ion exchangers 66.

A given voltage is applied from the power source 48 to between the processing electrodes 64a and the feeding electrodes 64b to carry out electrolytic processing of the conductive film (copper film 6) on the substrate W at the processing electrodes (cathodes) 64a through the action of hydrogen ions or hydroxide

ions generated by the ion exchangers 66. Though processing proceeds in the area of the substrate W facing the processing electrodes 64a, by moving the substrate W and the processing electrodes 64a relative to each other, processing of the entire surface of the substrate W can be effected. During processing, the substrate W is pressed against the ion exchangers 66 at a certain pressure, by supplying fluid into the pressure chamber 76. Specifically, the pressing force applied from the ion exchangers 66 to the substrate W is adjusted suitably by the fluid to be supplied into the pressure chamber 76 during the electrolytic processing of the substrate W. At this time, the electrode base 62 is supported floatingly by a floating mechanism 72, and moves vertically and tilts freely to a certain extent, thereby contacting the ion exchangers 66 of the electrode members 60 to the substrate W more uniformly over the entire surface of the substrate W.

The monitor 38 monitors the voltage applied between the processing electrodes 64a and the feeding electrodes 64b, or the electric current flowing therebetween to detect the end point (terminal of processing) during processing. It is noted in this connection that in electrolytic processing an electric current (applied voltage) varies, depending upon the material to be processed, even with the same voltage (electric current). For example, as shown in FIG. 8A, when an electric current is monitored in electrolytic processing of the surface of a substrate W to which a film of material B and a film of material A are laminated in this order, a constant electric current is observed during the processing of material A, but it changes upon the shift to the processing of the different material B. Likewise, when a voltage applied between the processing electrode and the feeding electrode is monitored, as shown in FIG. 8B, though a constant voltage is applied between the processing electrode and the feeding electrode during the processing of material A, the

voltage applied changes upon the shift to the processing of the different material B. FIG. 8A illustrates, by way of example, a case in which an electric current is harder to flow in electrolytic processing of material B compared to electrolytic processing of material A, and FIG. 8B illustrates a case in which the applied voltage becomes higher in electrolytic processing of material B compared to electrolytic processing of material A. As will be appreciated from the above-described example, the monitoring of changes in electric current or in voltage can surely detect the end point.

Though this embodiment shows the case where the monitor 38 monitors the voltage applied between the processing electrodes 64a and the feeding electrodes 64b, or the electric current flowing therebetween to detect the end point of processing, it is also possible to allow the monitor 38 to monitor a change in the state of the substrate being processed to detect an arbitrarily set end point of processing. In this case, "the end point of processing" refers to a point at which a desired processing amount is attained for a specified region in a surface to be processed, or a point at which an amount corresponding to a desired processing amount is attained in terms of a parameter correlated with a processing amount for a specified region in a surface to be processed. By thus arbitrarily setting and detecting the end point of processing even in the middle of processing, it becomes possible to conduct a multi-step electrolytic processing.

For example, the processing amount may be determined by detecting a change in frictional force due to a difference in friction coefficient produced when a different material is reached in a substrate, or a change in frictional force produced by removal of irregularities in the surface of the substrate. The end point of processing may be detected based on the processing amount thus determined. During electrolytic processing, heat

is generated by the electric resistance of the processing surface of a substrate, or by collision between water molecules and ions moving in the liquid (pure water) between the processing surface of the substrate and the processing electrodes. In processing e.g. a copper film deposited on the surface of a substrate under a controlled constant voltage, when a barrier layer or an insulating film becomes exposed with the progress of electrolytic processing, the electric resistance increases and the current value decreases, and the heat value decreases. Accordingly, the processing amount may be determined by detecting the change in the heat value. The end point of processing may therefore be detected. Alternatively, the film thickness of a to-be-processed film on a substrate may be determined by detecting a change in the intensity of reflected light due to a difference in reflectance produced when a different material is reached in the substrate. The end point of processing may be detected based on the film thickness thus determined. The film thickness of a to-be-processed film on a substrate may also be determined by generating an eddy current within a to-be-processed conductive film, for example a copper film, and monitoring the eddy current flowing within the substrate to detect a change in e.g. the frequency or the impedance of a sensor monitoring the eddy current, thereby detecting the end point of processing. Further, in electrolytic processing, the processing rate depends on the value of the electric current flowing between the processing electrode and the feeding electrode, and the processing amount is proportional to the quantity of electricity, determined by the product of the current value and the processing time. Accordingly, the processing amount may be determined by integrating the quantity of electricity, and detecting the integrated value reaching a predetermined value. The end point of processing may thus be detected.

After completion of the electrolytic processing, the power source 48 is disconnected from the processing electrodes 64a and the feeding electrodes 64b, and the rotation and the parallel movement of the substrate holder 42 are stopped. Thereafter, the substrate holder 42 is raised, and the substrate W is transferred to the transfer robot 36 after moving the arm 40. The transfer robot 36 takes the substrate W from the substrate holder 42 and, if necessary, transfers the substrate W to the reversing machine 32 for reversing it, and then transfers the substrate W to the cleaning section 39 for cleaning and drying it. The dried substrate W is then returned to the cassette in the loading/unloading unit 30.

Pure water, which is supplied between the substrate W and ion exchangers 66 during electrolytic processing, herein refers to a water having an electric conductivity of not more than 10 μS/cm. Ultrapure water refers to a water having an electric conductivity of not more than 0.1 μS/cm. The use of pure water or ultrapure water containing no electrolyte upon electrolytic processing can prevent extra impurities such as an electrolyte from adhering to and remaining on the surface of the substrate W. Further, copper ions or the like dissolved during electrolytic processing are immediately caught by the ion exchangers 66 through the ion-exchange reaction. This can prevent the dissolved copper ions or the like from re-precipitating on the other portions of the substrate W, or from being oxidized to become fine particles which contaminate the surface of the substrate W.

It is possible to use, instead of pure water or ultrapure water, a liquid having an electric conductivity of not more than 500 μS/cm or an electrolytic solution obtained by adding an electrolyte to pure water or ultrapure water. The use of an electrolytic solution can further lower the electric resistance and reduce the power consumption. A solution of a neutral salt

such as NaCl or Na_2SO_4, a solution of an acid such as HCl or H_2SO_4, or a solution of an alkali such as ammonia, may be used as the electrolytic solution, and these solutions may be selectively used according to the properties of the workpiece.

Further, it is also possible to use, instead of pure water or ultrapure water, a liquid obtained by adding a surfactant to pure water or ultrapure water, and having an electric conductivity of not more than 500 μS/cm, preferably not more than 50 μ S/cm, more preferably not more than 0.1 μ S/cm (resistivity of not less than 10 MΩ·cm). Due to the presence of a surfactant, the liquid can form a layer, which functions to inhibit ion migration evenly, at the interface between the substrate W and the ion exchangers 66, thereby moderating concentration of ion exchange (metal dissolution) to enhance the flatness of the processed surface. The surfactant concentration is desirably not more than 100 ppm.

Further, it is preferred to use an ion exchanger having an excellent water permeability as the ion exchanger 66 covering the surface of the electrode 64. By permitting pure water or ultrapure water to flow through the ion exchanger 66, a sufficient amount of water can be supplied to a functional group (sulfonic acid group in the case of a strongly acidic cation-exchange material) to thereby increase the amount of dissociated water molecules, and the processing products (including gasses) formed by the reaction between the to-be-processed material and hydroxide ions (or OH radicals) can be removed by the flow of water, whereby the processing efficiency can be enhanced. A water-permeable sponge-like member or a member in the form of a membrane, such as Nafion (trademark, DuPont Co.), having through-holes for permitting water to flow therethrough, for example, is used as such a water-permeable member.

The ion exchanger 66 may be composed of a non-woven fabric which has an anion-exchange group or a cation-exchange group.

A cation exchanger preferably carries a strongly acidic cation-exchange group (sulfonic acid group). However, a cation exchanger carrying a weakly acidic cation-exchange group (carboxyl group) may also be used. Though an anion exchanger preferably carries a strongly basic anion-exchange group (quaternary ammonium group), an anion exchanger carrying a weakly basic anion-exchange group (tertiary or lower amino group) may also be used.

The non-woven fabric carrying a strongly basic anion-exchange group can be prepared by, for example, the following method: A polyolefin non-woven fabric having a fiber diameter of 20-50 μm and a porosity of about 90% is subjected to the so-called radiation graft polymerization, comprising γ-ray irradiation onto the non-woven fabric and the subsequent graft polymerization, thereby introducing graft chains; and the graft chains thus introduced are then aminated to introduce quaternary ammonium groups thereinto. The capacity of the ion-exchange groups introduced can be determined by the amount of the graft chains introduced. The graft polymerization may be conducted by the use of a monomer such as acrylic acid, styrene, glicidyl methacrylate, sodium styrenesulfonate or chloromethylstyrene, or the like. The amount of the graft chains can be controlled by adjusting the monomer concentration, the reaction temperature and the reaction time. Thus, the degree of grafting, i.e. the ratio of the weight of the non-woven fabric after graft polymerization to the weight of the non-woven fabric before graft polymerization, can be made 500% at its maximum. Consequently, the capacity of the ion-exchange groups introduced after graft polymerization can be made 5 meq/g at its maximum.

The non-woven fabric carrying a strongly acidic cation-exchange group can be prepared by the following method: As in the case of the non-woven fabric carrying a strongly basic anion-exchange group, a polyolefin non-woven fabric having a

fiber diameter of 20-50 μm and a porosity of about 90% is subjected to the so-called radiation graft polymerization comprising γ-ray irradiation onto the non-woven fabric and the subsequent graft polymerization, thereby introducing graft chains; and the graft chains thus introduced are then treated with a heated sulfuric acid to introduce sulfonic acid groups thereinto. If the graft chains are treated with a heated phosphoric acid, phosphate groups can be introduced. The degree of grafting can reach 500% at its maximum, and the capacity of the ion-exchange groups thus introduced after graft polymerization can reach 5 meq/g at its maximum.

The base material of the ion exchanger 66 may be a polyolefin such as polyethylene or polypropylene, or any other organic polymer. Further, besides the form of a non-woven fabric, the ion exchanger may be in the form of a woven fabric, a sheet, a porous material, or short fibers, etc. When polyethylene or polypropylene is used as the base material, graft polymerization can be effected by first irradiating radioactive rays (γ-rays and electron beam) onto the base material (pre-irradiation) to thereby generate a radical, and then reacting the radical with a monomer, whereby uniform graft chains with few impurities can be obtained. When an organic polymer other than polyolefin is used as the base material, on the other hand, radical polymerization can be effected by impregnating the base material with a monomer and irradiating radioactive rays (γ-rays, electron beam and UV-rays) onto the base material (simultaneous irradiation). Though this method fails to provide uniform graft chains, it is applicable to a wide variety of base materials.

By using a non-woven fabric having an anion-exchange group or a cation-exchange group as the ion exchanger 66, it becomes possible that pure water or ultrapure water, or a liquid such as an electrolytic solution can freely move within the non-woven fabric and easily arrive at the active points in the non-woven

fabric having a catalytic activity for water dissociation, so that many water molecules are dissociated into hydrogen ions and hydroxide ions. Further, by the movement of pure water or ultrapure water, or a liquid such as an electrolytic solution, the hydroxide ions produced by the water dissociation can be efficiently carried to the surfaces of the processing electrodes 64a, whereby a high electric current can be obtained even with a low voltage applied.

When the ion exchanger 66 has only one of anion-exchange groups and cation-exchange groups, a limitation is imposed on electrolytically processible materials and, in addition, impurities are likely to form due to the polarity. In order to solve this problem, an anion exchanger carrying an anion-exchange group and a cation exchanger carrying a cation-exchange group may be superimposed, or the ion exchanger 66 may carry both of an anion-exchange group and a cation-exchange group per se, whereby a range of materials to be processed can be broadened and the formation of impurities can be restrained.

According to the electrolytic processing apparatus 34 of this embodiment, by adjusting the pressure of the fluid to be supplied into the pressure chamber 76, the pressure at which the substrate W contacts the ion exchangers 66 can be controlled with high precision. It is therefore possible to control the interfacial pressure between the substrate W and the ion exchangers 66 so that it is lower than a pressure at which a semiconductor device can be destroyed, making it possible to process the substrate without destroying a fragile material.

Further, according to the electrolytic processing apparatus 34 of the present invention, since a mechanical polishing action is not involved, a strong pressing by the substrate W as in CMP is not necessary. In the case where a fragile material is used as the interconnect material of the substrate W, it is preferred to adjust the pressure of the fluid

to be supplied into the pressure chamber 76 so that the pressure applied to the substrate W from the ion exchangers 66 becomes not more than 19.6 kPa (200 gf/cm^2, 2.9 psi), more preferably not more than 6.86 kPa (70 gf/cm^2, 1.0 psi), most preferably not more than 686 Pa (7 gf/cm^2, 0.1 psi), and carry out processing of the substrate W under such a low load.

The present invention is applicable to various types of electrolytic processing apparatus, and may be carried out by employing a variety of processing liquids and contact members.

FIG. 9 is a cross-sectional front view of an electrolytic processing apparatus according to another embodiment of the present invention, and FIG. 10 is a sectional view taken along the line A-A of FIG. 9. The electrolytic processing apparatus of this embodiment differs from the electrolytic processing apparatus of the preceding embodiment in the following respects.

The electrode section 46 includes a plurality of electrode members 60 each comprised of an electrode 64, which is to be connected to the cathode or the anode of the power source 48 to serve as a processing electrode 64a or feeding electrode 64b, and an ion exchanger 66 covering the upper surface of the electrode 64. The electrode members 60 are arranged on an electrode support base 63 in parallel at a given pitch, and are each floatingly supported on the electrode support base 63 independently by a floating mechanism 91. In particular, a pressure chamber 95 surrounded by an elastic membrane 93 is provided between each electrode member 60 and the electrode support base 63, and each pressure chamber 95 communicates with a pressurized fluid flow passage 62b formed in the interior of the electrode support base 63. Further, the pressurized fluid flow passage 62b is connected to a pressurized fluid supply passage 81 extending from a pressurized fluid supply source 78. Thus, each electrode member 60 is floatingly supported by the fluid pressure of the fluid enclosed within each respective pressure chamber 95. Further,

a stopper 97 is provided around each electrode member 60 for limiting the upward movement and the horizontal movement of the electrode member 60. The electrode member 60 may not necessarily be connected directly to the floating mechanism, but may be connected to it via a support member.

By thus supporting each respective electrode member 60, consisting of the electrode 64 and the ion exchanger 66, floatingly and independently on the electrode support base 63, the heights of the electrode members 60 from the electrode base 62 can be unified during processing so that the electrode members 60 can make contact with the substrate W more uniformly. This makes it possible to equalize the contact pressures of the electrode members 60 on the substrate W even when there are individual differences among the electrode members 60, such as variation in the thickness of ion exchanger 66, errors in the mounting of the ion exchanger 66, etc.

Around the substrate holder 42, on the other hand, there is disposed a rectangular tabular guide member 100, having a central hole 100a with a diameter corresponding to the diameter of the substrate holder 42, which is vertically movable by cylinders 104 coupled to a bracket 102 which is fixed to an arm 40. Tapered guide surfaces 100b, inclining outwardly and upwardly, are provided on either side of the lower surface of the guide member 100 in the direction perpendicular to the electrode members 60. When a substrate W and the electrode members 60 move relative to each other during processing, and an electrode member 60, positioned outside the guide member 100, moves to a processing position at which the electrode member 60 comes into contact with the substrate W, the electrode member 60, protruding upward due to the pressure in the pressure chamber 95, comes into contact at its upper surface with the guide surface 100b and lowers gradually while it is guided by the guide surface 100b, so that the electrode member 60 can move smoothly without

colliding against the outer peripheral end surface of the substrate.

Further, upon electrolytic processing, the lower surface, between the guide surfaces 100b, of the guide member 100 is made flush with the front surface (lower surface) of the substrate W held by the substrate holder 42 so that it becomes a contact surface 100c for contact with the ion exchangers 66 of the electrode members 60. Further, the outer shape of the guide member 100 is generally the same as the outer shape of the electrode section (assembly of the electrode members). Thus, the ion exchangers 60 of the electrode members 60 located at processing position, besides their contact with the substrate W, makes contact with the contact surface 100c of the rectangular guide member 100 outside the substrate W, so that as shown by the shaded portions in FIG. 10, the contact area of the ion exchangers 66 of the electrode members 60, which make contact with the substrate W to effect processing, with the substrate W and the contact surface 100c of the guide member 100 is always constant. This can prevent the pressure between the ion exchangers 66 and the substrate W in the contact portion from changing locally. In this connection, as described above, each electrode member 60 is pressed upward at a certain pressure via the pressure chamber 95. Accordingly, when a contact area between the ion exchanger 66 of the electrode member 60 and the substrate W becomes smaller, the contact pressure in that contact portion becomes large locally. Such a drawback can be avoided by making the contact area between the ion exchangers 66 of the electrode members 60 and the substrate W constant during electrolytic processing.

The present invention is not limited to electrolytic processing using an ion exchanger. For example, when an electrolytic solution is employed as a processing liquid, it is possible to attach to the surface of an electrode a scrubbing

member other than an ion exchanger, such as a soft polishing pad, for example POLYTEX pad (trademark, Rodel, Inc), a polyurethane sponge, a non-woven fabric, a foamed polyurethane or a PVA sponge.

In operation of the electrolytic processing apparatus of this embodiment, as with the preceding embodiment, the substrate W held by the substrate holder 42 is brought into contact with the surfaces of the ion exchangers 66 of the electrode members 60, and the substrate W is simultaneously rotated and reciprocated together with the substrate holder 42, while pure water or ultrapure water is supplied between the substrate W and the ion exchangers 66, and a given voltage is applied from the power source 48 to between the processing electrodes 64a and the feeding electrodes 64a, thereby carrying out electrolytic processing of the conductive film (copper film 6) on the substrate W. It is also possible, instead of continuously rotating the substrate, to rotate the substrate through a predetermined angle periodically to change the orientation relative to the long direction of the electrodes.

In the electrolytic processing, when an electrode member 60 positioned outside the guide member 100 moves to the processing position at which it makes contact with the substrate W, the electrode member 60, protruding upward due to the pressure in the pressure chamber 95, comes into contact at its upper surface with the contact surface 100b and lowers gradually while it is guided by the guide surface 100b, so that the electrode member 60 moves smoothly without colliding against the peripheral end surface of the substrate. Further, the ion exchangers 66 of the electrode members 60 located at processing postitions, other than those that contact the substrate W, make contact with the contact surface 100c of the rectangular guide member 100 outside the substrate W, so that the contact area of the ion exchangers 66 of the electrode members 60, which make contact with the

substrate W to effect processing, with the substrate W and the contact surface 100c of the guide member 100 is always constant. This prevents the pressure between the ion exchanger 66 and the substrate W in the contact portion from changing locally to cause an excess or deficiency in the processing amount.

The electrode base 62, on which the electrode members 60 are fixed, according to the preceding embodiment shown in FIGS. 5 through 7 may be replaced with the electrode support base 63, which supports each electrode member 60 floatingly by each respective floating mechanism 91, according to this embodiment shown in FIGS. 9 and 10. That is, it is possible to support the electrode support base 63, which supports each electrode member 60 by each respective floating mechanism 91, floatingly on the support base 70 by the floating mechanism with an adjustment member as shown in FIG. 7. In that case, the effect of floatingly supporting each electrode member 60 can be enhanced synergistically by the combination of the two floating mechanisms, i.e. the floating mechanism 91 for each electrode member 60 and the floating mechanism 72 for the electrode support base 63 that supports the plurality of electrode members 60.

FIG. 11 shows an electrolytic processing apparatus according to yet another embodiment of the present invention. The electrolytic processing apparatus of this embodiment differs from the electrolytic processing apparatus of the embodiment shown in FIGS. 9 and 10 in that the floating mechanism 91 for floatingly supporting each electrode member 60 comprises an elastic body 110, such as a rubber, a sponge, a porous resin or a non-woven fabric. The other construction is the same as the embodiment shown in FIGS. 9 and 10.

The internal pressure of the floating mechanism 91 shown in FIG. 9 and the modules of elasticity of the floating mechanism 91 shown in FIG. 11 may be changed every electrode by the adjustment member. For example, the rigidity of the floating

mechanisms 91 for part of the electrode members may be made higher (i.e. higher modules of elasticity), so that the pressing force from a substrate may be received mainly by those electrode members. In general, a more precise pressure adjustment is required on a processing electrode than a feeding electrode. Thus, it is possible to employ a higher-rigidity floating mechanism with less degree of floating for a feeding electrode member, or employ a floating mechanism only for a processing electrode member without floating a feeding electrode member. In that case, a processing electrode member floats sufficiently, and therefore a plurality of processing electrode members can make contact with a substrate at a uniform pressure. It is also possible to support a feeding electrode member by an elastic member and support a processing electrode member by a pressurized fluid chamber, thereby making the degree of floating (elasticity) higher for the processing electrode member.

FIG. 12 is a vertical sectional view showing a main portion of an electrolytic processing apparatus according to yet another embodiment of the present invention, and FIG. 13 is an enlarged view of a main portion of FIG. 12. As shown in FIG. 12, the electrolytic processing apparatus 600 includes a substrate holder 602 for holding a substrate W with its front surface facing downwardly, and a rectangular electrode section 604 provided below the substrate holder 602. The substrate holder 602, as with the substrate holder 42 of the preceding embodiments, is rotatable and movable vertically and horizontally. The electrode section 604 is provided with a hollow scroll motor 606 and, by the actuation of the scroll motor 606, makes a circular movement without rotation, a so-called scroll movement (translational rotary movement).

The electrode section 604 includes an electrode base 626 having a plurality of linearly-extending electrode members 608, and a vessel 610 which opens upwardly and serves as a support

base. The plurality of electrode members 608 are disposed in parallel at an even pitch on the electrode base 626. As with the electrolytic processing apparatus of the first embodiment described above, the electrode base 626 is floatingly supported on the vessel (support base) 610 by a floating mechanism. Positioned above the vessel 610, a liquid supply nozzle 612 is disposed for supplying a liquid, such as ultrapure water or pure water, into the vessel 610. The electrode members 608 each includes an electrode 614 to be connected to a power source in the apparatus. The electrodes 614 are connected alternately to the cathode and to the anode of the power source, that is, electrodes 614a are connected to the cathode of the power source and electrodes 614b are connected to the anode alternately. Thus, as described above, when processing copper, for example, the electrolytic processing action occurs on the anode side, and therefore the electrodes 614a connected to the cathode become processing electrodes and the electrodes 614b connected to the anode become feeding electrodes.

With respect to each processing electrode 614a connected to the cathode, as shown in detail in FIG. 13, an ion exchanger 616a composed e.g. of a non-woven fabric is mounted on the upper portion of the processing electrode 614a. The processing electrode 614a and the ion exchanger 616a are covered integrally with a second ion exchanger 618a composed of ion exchange membrane which shuts off permeation therethrough of a liquid and permits only ions to pass therethrough. Similarly, an ion exchanger 616b composed e.g. of a non-woven fabric is mounted on the upper portion of each feeding electrode 614b to be connected to the anode, and the feeding electrode 614b and the ion exchanger 616b are covered integrally with a second ion exchanger 618b composed of ion exchange membrane which shuts off permeation therethrough of a liquid and permits only ions to pass therethrough. Accordingly, ultrapure water or a liquid passes through

through-holes (not shown) provided at certain locations along the long direction of the electrode 614 and can move freely within the ion exchanger 616a, 616b composed of a non-woven fabric and easily reach the active points, having water dissociation catalytic activity, within the non-woven fabric, while the flow of the liquid is shut off by the ion exchanger 618a, 618b, which constitutes the below-described second partition.

A pair of liquid supply nozzles 620 is disposed on both sides of each processing electrode 614a connected to the cathode of the power source. In the interior of each liquid supply nozzle 620, a liquid flow passage 620a, extending in the long direction, is provided, and liquid supply holes 620b, which upward and communicate with the liquid flow passage 620a, are provided at certain locations along the long direction.

The processing electrode 614a and the pair of liquid supply nozzles 620 are integrated by a pair of tap bars 622, and held between a pair of insert plates 624 and fixed on the electrode base 626. On the other hand, the feeding electrode 614b, with its surface covered with the ion exchanger 618b, is held between a pair of holding plates 628 and fixed on the electrode base 626.

The ion exchangers 616a, 616b are, for example, composed of a non-woven fabric having an anion exchange group or a cation exchange group. As described above, it is possible to use a laminate of an anion exchanger having an anion exchange group and a cation exchanger having a cation exchange group, or impart both of anion exchange group and cation exchange group to the ion exchangers 616a, 616b themselves. A polyolefin polymer, such as polyethylene or polypropylene, or other organic polymers may be used as the base material of the ion exchangers. With respect to the base material of the electrodes 614 of the electrode members 608, rather than metals or metal compounds widely used for electrodes, it is preferred to use carbon, a relatively

inactive noble metal, a conductive oxide or a conductive ceramic, as also described above.

A partition 630a, composed of e.g. a resin having elasticity, is mounted on the upper surface of each liquid supply nozzle 620 over the full length in the long direction. A thickness of the partition 630 is set at such a thickness that when the substrate W held by the substrate holder 602 is brought close to or into contact with the ion exchangers 618a, 618b of the electrode members 608 to carry out electrolytic processing of the substrate W, the upper surface of the partition 630 comes into pressure contact with the substrate W held by the substrate holder 602. Accordingly, upon electrolytic processing, flow paths 632 formed between the processing electrodes 614a and the substrate W, and flow paths 634 formed between the feeding electrodes 614b and the substrate W, which are separated by the partitions 630, are formed in parallel between the electrode section 604 and the substrate holder 602. Further, each flow path 632 formed between the processing electrode 614a and the substrate W is separated into two flow paths 632a, 632b by the ion exchanger 618a as a second partition composed of an ion exchange membrane, while each flow path 634 formed between the feeding electrode 614b and the substrate W is separated into two flow paths 634a, 634b by the ion exchanger 618b as a second partition composed of an ion exchange membrane.

According to this embodiment, upon electrolytic processing, the vessel 610 is filled with a liquid, such as ultrapure water or pure water, supplied from the liquid supply nozzle 612, while a liquid, such as ultrapure water or pure water, is supplied from the through-holes (not shown) provided in the electrodes 614 to the ion exchangers 616a, 616b composed of a non-woven fabric disposed on the upper portions of the processing electrodes 614a and the feeding electrodes 614b. An overflow channel 636 for discharging the liquid that has overflowed a

circumferential wall 610a of the vessel 610 is provided outside the vessel 610. The liquid that has overflowed the circumferential wall 610a flows through the overflow channel 636 into a waste liquid tank (not shown).

In this embodiment, a pair of liquid supply nozzles having liquid supply holes provided at certain locations along the long direction is disposed on both sides of each processing electrode, and a liquid is supplied form the liquid supply nozzles. With this arrangement, it becomes possible to more securely control the flow of the liquid flowing along the flow paths 632 formed between the processing electrodes 614a and the substrate W and the flow of the liquid flowing along the flow paths 634 formed between the feeding electrodes 614b and the substrate, and decrease the amount of the liquid that flows across the partitions into the adjacent spaces. It is also possible to make a flow of the liquid flowing along electrodes by pushing out the liquid along the long direction of the electrodes.

In the above-described embodiments which use an ion exchanger mounted on an electrode, the shape of electrode and the liquid for processing are not particularly limited. A contact member or a partition may be provided between adjacent electrodes. Thus, the shape of the electrode is not limited to a rod shape, but any shape may be selected that is suited for workpiece-facing arrangement of a plurality of electrodes. It is possible to mount a liquid-permeable or liquid-impregnable scrubbing member other than an ion exchanger to an electrode. Further, the contact member or the partition, provided between adjacent electrodes, may be made higher than the electrodes so as to avoid direct contact between a workpiece and the electrodes, which makes it possible to expose the surfaces of the electrodes. Even in the case of not mounting an ion exchanging on an electrode,

it is preferred to provide the second partition for separating the flow of a fluid between a workpiece and electrodes. It is also possible to fix the second ion exchanger 618 on each electrode, and allow each electrode to float as in the second embodiment.

The above-described embodiments, in principle, are directed to correcting non-uniform processing due to individual differences among electrodes by correcting non-uniformity in the contact pressure of each electrode on a substrate, without providing a floating mechanism on the side of a substrate holder (top ring). It is, however, possible to provide a floating mechanism also on the top ring side.

FIG. 14 is a vertical sectional view showing an electrolytic processing apparatus according to yet another embodiment of the present invention. The apparatus of this embodiment differs from the apparatus shown in FIGS. 5 through 7 in the following respects.

The hollow motor 160 is disposed below the electrode section 46. A drive end 164 is formed at the upper end portion of the main shaft 162 of the hollow motor 160 and arranged eccentrically position to the center of the main shaft 162. The electrode section 46 is rotatably coupled to the drive end 164 via a bearing (not shown) at the center portion thereof. Three or more of rotation-prevention mechanisms are provided in the circumferential direction between the electrode section 46 and the hollow motor 160.

FIG. 15A is a plan view showing the rotation-prevention mechanisms of this embodiment, and FIG. 15B is a cross-sectional view taken along the line A-A of FIG. 15A. As shown in FIGS. 15A and 15B, three or more (four in FIG. 15A) of rotation-prevention mechanisms 166 are provided in the circumferential direction between the electrode section 46 and the hollow motor 160. As shown in FIG. 15B, a plurality of depressions 168, 170 are formed at equal intervals in the

circumferential direction at the corresponding positions in the upper surface of the hollow motor 160 and in the lower surface of the electrode section 46. Bearings 172, 174 are fixed in each depression 168, 170, respectively. A connecting member 180, which has two shafts 176, 178 that are eccentric to each other by eccentricity "e", is coupled to each pair of the bearings 172, 174 by inserting the respective ends of the shafts 176, 178 into the bearings 172, 174. The eccentricity of the drive end 164 against to the center of the main shaft 162 of the hollow motor 160 is also "e". Accordingly, the electrode section 46 is allowed to make a revolutionary movement with the distance between the center of the main shaft 162 and the drive end 164 as radius "e", without rotation about its own axis, i.e. the so-called scroll movement (translational rotation movement) by the actuation of the hollow motor 160.

Next, the electrode section 46 according to this embodiment will now be described. The electrode section 46 of this embodiment includes a plurality of electrode members 82. FIG. 16 is a plan view of the electrode section 46 of this embodiment, FIG. 17 is a sectional view taken along the line B-B of FIG. 16, and FIG. 18 is an enlarged view of a portion of FIG. 17. As shown in FIGS. 16 and 17, the electrode section 46 includes a plurality of electrode members 82 extending in the X direction (see FIG. 16), and the electrode members 82 are disposed in parallel on a tabular base 84.

As shown in FIG. 18, each electrode member 82 comprises an electrode 86 to be connected to the power source 48 (see FIG. 14), an ion exchanger (ion exchange membrane) 90 covering the surface of the electrode integrally. The ion exchanger 90 is mounted to the electrode 86 by holding plates 85 disposed on both sides of the electrode 86.

The ion exchangers 90 should meet the following four requisites:

(1) Removal of processing products (including a gas)

This is closely related to stability of the processing rate and evenness in the distribution of processing rate. To meet this demand, it is preferable to use an ion exchanger having "water permeability" and "water-absorbing properties". By the term "water permeability" is herein meant a permeability in a broad sense. Thus, the member, which itself has no water permeability but can permit permeation therethrough of water by the provision of holes or grooves, is herein included as a "water-permeable" member. The term "water-absorbing properties" means properties of absorbing water and allowing water to penetrate into the material.

(2) Stability of processing rate

To meet this demand, it is desirable to use a multi-layer laminated ion exchanger, thereby securing an adequate ion-exchange capacity.

(3) Flatness of processed surface (ability of eliminating steps)

To meet this demand, the processing surface of the ion exchanger desirably has a good surface smoothness. Further, in general, the harder the member is, the flatter is the processed surface (ability of eliminating steps).

(4) Long life

In the light of long mechanical life of the member, it is desirable to use an ion-exchange material having a high wear resistance.

It is preferred that the ion exchanger 90 has a high hardness and a good surface smoothness. According to this embodiment, Nafion (trademark, DuPont Co.) with a thickness of 0.2 mm is employed. The term "high hardness" herein means high rigidity and low modulus of elasticity against compression. A material having a high hardness, when used in processing of a workpiece having fine irregularities in a surface, such as an interconnect patterned wafer, hardly follows the irregularities and is likely

to selectively remove the raised portions of the pattern. The expression "has a surface smoothness" herein means that the surface has few irregularities. An ion exchanger having a surface smoothness is less likely to contact the recesses in a surface of a workpiece, such as an interconnect patterned wafer, and is more likely to selectively remove the raised portions of the pattern.

It is preferable to use an ion exchanger having good water permeability as the ion exchanger 90. By allowing pure water or ultrapure water to flow within the ion exchanger 90, a sufficient amount of water can be supplied to a functional group (sulfonic acid group in the case of an ion exchanger carrying a strongly acidic cation-exchange group) thereby to increase the amount of dissociated water molecules, and the process product (including a gas) formed by the reaction with hydroxide ions (or OH radicals) can be removed by the flow of water, whereby the processing efficiency can be enhanced. The flow of pure water or ultrapure water is thus necessary, and the flow of water should desirably be constant and uniform. The constancy and uniformity of the flow of water lead to constancy and uniformity in the supply of ions and the removal of the process product, which in turn lead to constancy and uniformity in the processing.

As described above, the ion exchangers 90 may be composed of a non-woven fabric which has an anion-exchange group or a cation-exchange group.

According to this embodiment, the electrodes 86 of adjacent electrode members 82 are connected alternately to the cathode and to the anode of the power source 48. For example, electrodes 86a (see FIG. 17) are connected to the cathode of the power source 48 and electrodes 86b (see FIG. 17) are connected to the anode. When processing copper, for example, the electrolytic processing action occurs on the cathode side, and therefore the electrode 86a connected to the cathode becomes a processing electrode,

and the electrode 86b connected to the anode becomes a feeding electrode. Thus, according to this embodiment, the processing electrodes 86a and the feeding electrodes 86b are disposed in parallel and alternately.

In the case where the processing material is a conductive oxide such as tin oxide or indium tin oxide (ITO), electrolytic processing is carried out after reducing the processing material. More specifically, with reference to FIG. 14, the electrodes connected to the anode of the power source 48 serve as reduction electrodes and the electrodes connected to the cathode serve as feeding electrodes to effect reduction of the conductive oxide. Subsequently, processing of the reduced conductive material is carried out by making the previous feeding electrodes serve as the processing electrodes. Alternatively, the polarity of the reduction electrodes at the time of reduction of the conductive oxide may be reversed so that the reduction electrodes can serve as the processing electrodes. Removal processing of the conductive oxide may also be effected by making the processing material serve as a cathode and allowing it to face an anode electrode.

According to the above-described embodiment, though a copper film 6 (see FIG. 1B) as a conductor film formed in the surface of the substrate is processed by electrolytic processing, an unnecessary ruthenium (Ru) film formed on or adhering to the surface of a substrate may be processed (etched and removed) by electrolytic processing in the same manner by making the ruthenium film serve as a anode and the electrodes connected to the cathode serve as processing electrodes.

By thus providing the processing electrodes 86a and the feeding electrodes 86b alternately in the Y direction of the electrode section 46 shown in FIG. 16 (direction perpendicular to the long direction of the electrode members 82), provision of a feeding section for feeding electricity to the conductive

film (to-be-processed material) of the substrate W is no longer necessary, and processing of the entire surface of the substrate becomes possible. Further, by changing the positive and negative of the voltage applied between the processing electrodes 86a and the feeding electrodes 86b in a pulse form, it becomes possible to dissolve the electrolysis products, and improve the flatness of the processed surface through the multiplicity of repetition of processing.

As shown in FIG. 17, a flow passage 92 for supplying pure water, more preferably ultrapure water, to the to-be-processed surface is formed in the interior of the base 84 of the electrode section 46, and the flow passage 92 is connected to a pure water supply source (not shown) via a pure water supply pipe 94. On both sides of each electrode member 82, there are provided pure water jet nozzles 96 for jetting the pure water or ultrapure water supplied from the flow passage 92 to between the substrate W and the ion exchangers 90 of the electrode members 82. In each pure water jet nozzle 96, a plurality of jet ports 98 are provided along the X direction (see FIG. 16) for jetting pure water or ultrapure water toward the to-be-processed surface of the substrate W facing the electrode members 82, i.e., the portion of the substrate W in contact with the ion exchangers 90. Pure water or ultrapure water in the flow passage 92 is supplied from the jet ports 98 of the pure water jet nozzles 96 to the entire to-be-processed surface of the substrate W. As shown in FIG. 18, the height of each pure water jet nozzle 96 is lower than the height of the ion exchanger 90 of each electrode member 82, so that the top of the pure water jet nozzle 96 does not contact the substrate W upon contact of the substrate W with the ion exchanger 90 of the electrode member 82.

As shown in FIG. 18, round chamfered portions 202 are provided at both edges of the substrate-facing surface of the electrode 86 of each electrode member 82. The ion exchanger

90, with its round portions conforming to the shape of the chamfered portions 202, covers the surfaces of the chamfered portions 202. The provision of the round chamfered portions 202 at the edges of the substrate-facing surface of the electrode 86 can lessen the electric field concentration on the edge portions and thereby extend the life of the ion exchanger 90.

In particular, when carrying out processing with an electrode 86, having no round edge portion in the substrate-facing surface, covered with the ion exchanger 90 by applying a given voltage so that electrodes 86a connected to the cathode of the power source 48 becomes processing electrodes while electrodes 86b connected to the anode becomes feeding electrodes, the electric field concentrates particularly on the edge portion A of the substrate-facing surface of the electrode 86, as shown in FIG. 19. Processing products (copper ions and copper oxide) accumulate preferentially in the edge portion A of the electrode 86 on which the electric field concentrates. This results in a short circuit and makes it impossible to use up the whole ion-exchange capacity of the ion exchanger 90. In this regard, when the processing products accumulated in the ion exchanger 90 have reached the processing surface of the substrate W and a short circuit occurs, processing does not proceed any more or becomes non-uniform. Further, such an ion exchanger can be regenerated with difficulty (difficult to remove the deposits by a regeneration operation). Accordingly, the ion exchanger 90 must be regarded as having come to the end of its life despite its unused ion-exchange capacity, and must be changed for a new one.

According to this embodiment, on the other hand, the round chamfered portions 202 are provided at the edges of the substrate-facing surface of the electrode 86. This can lessen the electric field concentration on the chamfered portions 202 and can therefore reduce the above-described local accumulation

of processing products in the ion exchanger 90, thereby extending the life of the ion exchanger 90.

Through-holes 200, communicating with the flow passage 92 and the ion exchanger 90, are formed in the interior of the electrode 86 of each electrode member 82. With this arrangement, pure water or ultrapure water in the flow passage 92 is supplied through through-holes 200 to the ion exchanger 90.

According to the electrolytic processing apparatus of this embodiment, the substrate W held by the substrate holder 42 is brought close to or into contact with the surfaces of the ion exchangers 90 of the electrode section 46. Thereafter, the substrate-rotating motor 58 is driven to rotate the substrate W and, at the same time, the hollow motor 160 is driven to allow the electrode section 46 to make a scroll movement, while pure water, preferably ultrapure water is jetted from the jet ports 98 of each pure water jet nozzle 96 to between the substrate W and each electrode member 82, and pure water or ultrapure water is supplied through each through-hole 200 into the ion exchanger 90. According to this embodiment, pure water or ultrapure water which has been supplied to the ion exchanger 90 is discharged from the ends in the long direction of each electrode member 82. A given voltage is applied so that electrodes 86a connected to the cathode of the power source 48 become processing electrodes while electrode 86b connected to the anode become feeding electrodes, and electrolytic processing of the conductive film (copper film 6) on the substrate W is effected at the processing electrodes (cathodes) through the action of hydrogen ions or hydroxide ions generated by the ion exchangers 90.

According to this embodiment, the reciprocating motor 56 is driven to move the arm 40 and the substrate holder 42 in the Y direction during electrolytic processing. Thus, according to this embodiment, processing is carried out while allowing the electrode section 46 to make a scroll movement and moving

the substrate W in the direction perpendicular to the long direction of the electrode members 82. It is, however, possible to allow the substrate W to make a scroll movement while moving the electrode section 46 in the direction perpendicular to the long direction of the electrode members 82. It is also possible to employ a reciprocating linear movement in the Y direction instead of the scroll movement.

With the progress of electrodes processing, processing products, such as copper ions and copper oxide, are taken and accumulated in the ion exchanger 90. As described above, by the provision of the round chamfered portions 202 at the edges of the substrate-facing surface of the electrode 86 to lessen the electric field concentration on the chamfered portions 202, the local accumulation of the processing products in the ion exchanger 90 can be reduced, whereby the life of the ion exchanger 90 can be extended.

When using a liquid, like ultrapure water, which itself has a large resistivity, it is preferred to bring the ion exchanger 90 into "contact" with the surface of the substrate W. This can lower the electric resistance, lower the voltage applied, and reduce the power consumption. Thus, the "contact" does not imply "press" for giving a physical energy (stress) to a workpiece as in CMP, for example. Accordingly, the electrolytic processing apparatus of this embodiment employs the vertical-movement motor 50 for bringing the substrate W into contact with or close to the electrode section 46, and does not have such a press mechanism as usually employed in a CMP apparatus that presses aggressively a substrate against a polishing member. In this regard, according to a CMP apparatus, a substrate is pressed against a polishing surface generally at a pressure of about 20-50 kPa, whereas in the electrolytic processing apparatus of this embodiment, the substrate W may be contacted with the ion exchanger 90 at a pressure of less than 20 kPa.

Even at a pressure less than 10 kPa, a sufficient removal processing effect can be achieved.

Though this embodiment uses the electrode member 82 which, as shown in FIG. 20A, consists of the electrode 86 having the round chamfered portions 202 at the edges of the substrate-facing surface, and the ion exchanger 90 integrally covering the electrode 86, it is also possible to use electrode members as shown in FIGS. 20B and 20C. In particular, the electrode member 182 shown in FIG. 20B uses, as an electrode 186 to be connected to the power source 48 (see FIG. 14), a long electrode with a narrow width S, having a rectangular cross-section, whose substrate-facing surface 188 has a semicircular shape. The surface of the electrode 186 is covered integrally with an ion exchanger 190. In the case of using the long electrode 186 having a narrow width, by making the entire substrate-facing surface 188 semicircular, it becomes possible to reduce the local accumulation of processing products in the ion exchanger 190 covering the electrode 186 and narrow that area of the ion exchanger 190 which comes close to or into contact with the substrate W.

The electrode member 182a shown in FIG. 20C uses, as an electrode 186a to be connected to the power source 48 (see FIG. 14), a long electrode having a circular cross-section. The surface of the electrode 186a is covered integrally with an ion exchanger 190a. The use of such an electrode member can also reduce the local accumulation of processing products in the ion exchanger 190a covering the electrode 186a and narrow that area of the ion exchanger 190a which comes close to or into contact with the substrate W.

FIGS. 21A through 21D show the main portions of various electrode members for use in an electrolytic processing apparatus according to yet another embodiment of the present invention. The electrode member 282 shown in FIG. 21A is

comprised of an electrode 286 to be connected to the power source 48 (see FIG. 14), an insulator 292 formed integrally on the substrate-facing surface of the electrode 286, and an ion exchanger 290 integrally covering the surfaces of the electrode 286 and the insulator 292. The insulator 292 has round chamfered portions 294 at the edges of the substrate-facing surface.

As described above, when the ion exchanger 290 is provided such that it covers each electrode 286 and processing of the substrate W is carried out by applying a voltage between the electrodes (processing electrodes and feeding electrodes), the electric field concentrates on the surface, facing the substrate W, of the electrodes 286. The processing products (copper ions and copper hydroxide) accumulate preferentially in that portion of the ion exchanger 290 which is close to or in contact with the substrate-facing surface of the electrode 286. According to the electrode member 282, the insulator 292 is interposed between the substrate-facing surface of the electrode 286 and the ion exchanger 290, thereby eliminating the electric field concentration on the substrate-facing surface of the electrode 286. Further, the presence of the insulator 292 makes the substrate-facing surface of the electrode 286 farther from the substrate W. This makes it possible to use up the ion-exchange capacity of that portion of the ion exchanger 290 which is positioned between the substrate W and the substrate-facing surface of the electrode 286, thereby extending the life of the ion exchanger 290.

The electrode member 282a shown in FIG. 21B, similarly to the electrode member shown in FIG. 20B, uses as an electrode 286a to be connected to the power source 48 (see FIG. 14) a long electrode having a narrow width and a rectangular cross-section. An insulator 292a having a semicircular top portion is formed integrally on the substrate-facing surface of the electrode 286a. The surfaces of the electrode 286a and the insulator 292a are

covered integrally with an ion exchanger 290a.

The electrode member 282b shown in FIG. 21C, similarly to the electrode member shown in FIG. 20C, uses as an electrode 286b to be connected to the power source 48 (see FIG. 14) a long electrode having a semicircular cross-section. An insulator 292b having a semicircular cross-section is formed integrally on the substrate-facing surface of the electrode 286b such that the insulator 292b, together with the electrode 286b, forms a perfect circle. The surfaces of the electrode 286b and the insulator 292b are covered integrally with an ion exchanger 290b.

The electrode member 282c shown in FIG. 21D uses, as an electrode 286c to be connected to the power source (see FIG. 14), a long electrode having a narrow width and a rectangular cross-section. An insulator 292c having a semicircular top portion is formed integrally on the substrate-facing surface of the electrode 286c. The insulator 292c, except the top portion, and the electrode 286c are covered with ion exchangers 296 composed of, for example, a C-membrane. Further, the top portion of the insulator 292b and the ion exchangers 296 are covered integrally with an ion exchanger 290c composed of, for example, Nafion (trademark, DuPont Co.). By thus interposing the ion exchangers 296 between the electrode 286c and the ion exchanger 290c which is to make contact with the substrate W, the total ion-exchange capacity can be increased.

The electrode members shown in FIGS. 21B through 21D, as with the electrode member shown in FIG. 21A, can eliminate the electric field concentration on the substrate-facing surfaces of the electrodes 286a, 286b, 286c. Further, the presence of the respective insulators 292a, 292b, 292c makes the substrate-facing surfaces of the electrodes 286a, 286b, 286c farther from the substrate W. This makes it possible to use up the ion-exchange capacities of those portions of the ion exchangers 290a, 290b, 290c which are positioned between the

substrate W and the substrate-facing surfaces of the electrodes 286a, 286b, 286c, thereby extending the lives of the ion exchangers 290a, 290b, 290c.

According to the electrode members shown in FIGS. 21A through 21D, the insulators 292, 292a, 292b, 292c are respectively formed integrally with the electrodes 286, 286a, 286b, 286c to facilitate the production of the electrode members, and the presence of the insulators 292, 292a, 292b, 292c can make the substrate-facing surfaces of the electrodes 286, 286a, 286b, 286c apart from the substrate W at a desired distance. It is, however, also possible to cover the substrate-facing surfaces of the electrodes 286, 286a, 286b, 286c with e.g. a highly insulative vinyl tape.

FIG. 22 shows an electrode member for use in an electrolytic processing apparatus according to yet another embodiment of the present invention. The electrode member 382 of this embodiment employs a composite ion exchanger 390 consisting of a first ion exchanger 390a superimposed on the upper surface of an electrode 386 and a second ion exchanger (ion-exchange membrane) 390b integrally covering the electrode 386 and the first ion exchanger 390a. The entire surface of the electrode 386, except the central portion of the substrate-facing surface, i.e. the edge portions and the side surfaces of the electrode 386, is covered with an insulator 392 so that the electrode 386 and the second ion exchanger 390b are insulated from each other.

It is preferred to use as the first ion exchanger 390a an ion exchanger having a high ion-exchange capacity. According to this embodiment, a non-woven fabric ion exchanger with a thickness of 1 mm is employed to increase the total ion-exchange capacity of the ion exchanger 390. This can increase the total amount of the processing products (copper oxide and copper ions), produced by the electrolytic reaction, that can be accumulated in the ion exchanger 390.

It is preferred that at least the second ion exchanger 390b which is to face a workpiece have high hardness and good surface smoothness, as described above. According to this embodiment, Nafion (trademark, DuPont CO.) with a thickness of 0.2 mm is employed. By thus combining the second ion exchanger 390b having good surface smoothness with the first ion exchanger 390a having a large ion exchange capacity, the defect of small ion exchange capacity of the second ion exchanger 390b can be compensated for by the first ion exchanger 390a, and the ion-exchange capacity of the ion exchanger 390 as a whole can be increased.

In the case of using the composite ion exchanger 390 comprising the plurality of ion exchangers 390a, 390b like this embodiment, if the outer second ion exchanger 390b to be close to or in contact with the substrate W is in contact with the electrode 386, as shown in FIG. 23, an electric current flows preferentially in the outer second ion exchanger (ion-exchange membrane) 390b, e.g. of Nafion, and therefore the processing products accumulate locally in the ion exchanger (ion-exchange membrane) 390b in a concentrated manner. This makes it impossible to use up the total ion-exchange capacity of the composite ion exchanger 390 including the other ion exchanger 390a. This drawback is marked especially with a thin ion-exchange membrane having a small ion-exchange capacity, such as Nafion.

According to this embodiment, the electrode 386 and the second ion exchanger 390b to be close to or in contact with the substrate W are at least partly insulated from each other by the insulator 392. This can prevent an electric current from flowing preferentially in the second ion exchanger 390b which is close to or in contact with the substrate W, thereby extending the life of the composite ion exchanger 390 including the other ion exchanger 390a.

FIGS. 24A through 24C show various electrode members for

use in an electrolytic processing apparatus according to yet another embodiment of the present invention. The electrode member shown in FIG. 24A employs a composite ion exchanger 490 consisting of a first ion exchanger 490a which is a multi-layer (four-layer) laminate of, for example, C-membranes (non-woven fabric ion exchangers) having a high ion-exchange capacity, superimposed on the upper surface of an electrode 486, and a second ion exchanger (ion-exchange membrane) 490b, for example Nafion, integrally covering the electrode 486 and the first ion exchanger 490a. The entire surface of the electrode 486, except the central portion of the substrate-facing surface, is covered with an insulator 492 so that the electrode 486 and the second ion exchanger 490b are insulated from each other.

The use as the first ion exchanger 490a of a multi-layer laminate of e.g. C-membranes (non-woven fabric ion exchangers) having a high ion exchange capacity can further increase the total ion-exchange capacity of the whole ion exchanger 490.

The electrode member shown in FIG. 24B differs the electrode member shown in FIG. 24A in that the entire surface of the multi-layer first ion exchanger 490a, except the substrate-facing surface, is covered with a second insulator 492a so that the first ion exchanger 490a and the second ion exchanger 490b are insulated from each other by the second insulator 492a. The other construction is substantially the same as the electrode member shown in FIG. 24A.

In the case of using the plurality of ion exchangers 490a, 490b, the accumulation or growth of processing products proceeds preferentially in the lowermost layer of the first ion exchanger 490a in contact with the electrode 486. If the peripheral portion of the lowermost layer of the first ion exchanger 490a is in contact with the second ion exchanger 490b, as in the electrode member shown in FIG. 24A, a processing product P_1 accumulated in the lowermost layer of the first ion exchanger 490a spreads

toward the second ion exchanger 490b close to or in contact with a substrate, and a processing product P_2 accumulates at the interface between the lowermost layer of the first ion exchanger 490a and the second ion exchanger 490b. A processing product P_3 then accumulates in the second ion exchanger 490b, leading to a short circuit.

According to the electrode member shown in FIG. 24B, on the other hand, the electrode 486 and the second ion exchanger 490b to be close to or in contact with a substrate W are insulated by the insulator 492 from each other, and the second ion exchanger 490b and the first ion exchanger 490a are insulated by the second insulator 492a from each other. Accordingly, the processing product, accumulated in the lowermost layer of the first ion exchanger 490a, grows and accumulates in the overlaying layer of the first ion exchanger 490a, without diffusing into the second ion exchanger 490b close to or in contact with the substrate W. After the processing product has accumulated in the whole first ion exchanger 490a, it begins to accumulate in the second ion exchanger 490b. The life of the whole ion exchanger 490 can thus be extended.

As shown in FIG. 24C, insulation between the electrode member 486 and the second ion exchanger 490b to be close to or in contact with a substrate W as well as insulation between the second ion exchanger 490b and the first ion exchanger 490a may be made integrally by a cylindrically-extending insulator 492c.

As described hereinabove, according to the present invention, unlike a CMP processing, electrolytic processing of a workpiece, such as a substrate, can be effected through an electrochemical action without causing any physical defects in the workpiece that would impair the properties of the workpiece. Further, the present electrolytic processing apparatus and method can effectively remove (clean) matter adhering to the surface of the workpiece. Accordingly, the present invention